Natural attenuation of heavy metals and arsenic in Fe-rich soils: A case study

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Fe-and Mn-oxides are used as soil amendments to reduce the mobility and bioavailability of contaminant metals without drastically altering the physical or chemical properties of the soil. When these oxides, which are reactive for trace metals, are naturally abundant in soil, they may provide a natural way of in situ stabilization of heavy metals in the soil.
Wastewater discharge from the processing of phosphate ores has contributed to pollution by heavy metals and As in soils adjoining the Grote Beek river (15km long) in the Northeastern part of the province of 'Vlaams-Brabant' (Central Belgium). Moreover, the effluents of a polyvinylchloride plant generate chloride concentrations comparable to concentrations in seawater. The study area is characterized by sandy soils and underlain by the Diestian formation, containing between 30-40% glauconite. Organic- and iron-rich wetland soils have developed along this stream. The river follows a very meandering path and as a consequence several flooding zones occur along the river, which are flooded a few times a year during periods of heavy rainfall. Heavy metal mobility was investigated in three representative samples, (a soil sample rich in iron and organic material (FO), dredged sediment (DR) and a clayey (glauconite) overbank sediment (OB)), polluted with Cd, As, Zn, Cr, Ba and Ni (Table 1).
A modification of the BCR-extraction scheme (Quevauviller et al., 1994), optimized for Fe-rich samples, was applied. pH_{stat} leaching tests as described by Van Herreweghe et al. (2002) (pH 2, 4, 6, 8 and 10) were performed on these samples. Leaching behaviour was modeled with a thermodynamic speciation model (MINTEQA2). The observation of the leaching of metals as a function of time also provided information on reaction kinetics. Since chlorocomplexes of heavy metals, especially of Cd substantially increase their mobility in soil (Hahne and Kroontje, 1973), the influence of chlorides on the leaching of heavy metals was investigated in batch tests.

Table 1: Concentrations of heavy metals, As, Fe, organic carbon (org. C) pH, in the 3 studied samples (OB=overbank sediment, DR= dredged sediment, FO= soil sample rich in Fe and organic material).

	Cr	Ni	Cu	Zn	As	Cd	Ba	Pb	Fe	Org C	pH
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%	
OB	272	20	17	506	92	11	62	29	11,96	>3	6,4
DR	84	84	182	4083	254	213	753	33	8,23	8,8	6,8
FO	44	30	10	265	176	40	292	56	9,73	9,0	6,3

Fe-oxides play an important role in the binding of heavy metals and As in the alluvial sediments of the Grote Beek river. In the studied samples As, Cr, Ba and Pb for the greater part seem to be incorporated in poorly reactive Fe-oxides, which provide a natural way of in situ stabilization of these metals. Organic matter only plays a minor role in the binding of Cr, Ni, Cu and Pb. Cd, Zn, Ni and Cu are merely adsorbed to Fe-oxides/clay or incorporated in less stable Fe-oxides. As a consequence, reducing conditions caused by periodical flooding may induce the mobilization of latter elements. In the dredged sediments (DR), Ca-carbonates as well are a sink for Cd, Zn, Ba and Ni and provide an excellent acid buffering capacity. Leaching at pH 6 (= close to soil pH)

was almost negligible for most elements, indicating the low mobility of these elements at the moment. The mobilization of Cu, Zn, Cd and Ni by chlorides decreased in the order Cu>Zn>Cd>Ni and was the most important for the dredged sediment. Although total metal concentrations in the three samples differ considerably, the amount of metals leached are rather low and in the same order of magnitude for the different samples (Cd: 0.45-1.04 mg/kg, Zn: 1.07-3.29 mg/kg, Cu: 2.23-3.35 mg/kg, Ni: 0.09-0.97 mg/kg).

Further investigations will focus on the effect of reducing conditions, brought about by periodically flooding, on the mobility of heavy metals and As.

References

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